

The rotational a -type spectrum of [^{13}C]diazirine, H_2CN_2



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The rotational spectrum of ^{13}C isotopically enriched diazirine, $\text{H}_2^{13}\text{C}^{14}\text{N}_2$, has been recorded in the region between 12 and 250 GHz. From an analysis of the nuclear hyperfine structure of the rotational transitions, quadrupole coupling and spin-rotational constants have been determined. Using Watson's A -reduced Hamiltonian, the rotational constants, the quartic and some sextic centrifugal distortion constants have been obtained for the ground vibrational state. The rotational constants obtained are

$$\begin{aligned} A &= 40\,950.3414 \text{ MHz}, \\ B &= 22\,869.8200 \text{ MHz}, \\ C &= 16\,322.6670 \text{ MHz} \end{aligned}$$

The nuclear quadrupole coupling constants and the spin-rotation constants are

$$\begin{aligned} \chi_{aa} &= -0.665 \text{ MHz} & C_{aa} &= 11.1 \text{ kHz} \\ \chi_{bb} &= -2.695 \text{ MHz} & C_{bb} &= 6.1 \text{ kHz} \end{aligned}$$

for the two identical quadrupole nitrogen nuclei. The accuracy of the constants obtained allows us to evaluate the line positions and hyperfine structure of any rotational transition in the microwave and millimetre wave region.

Le spectre rotationnel de la diazirine isotopiquement enrichie en ^{13}C , $\text{H}_2^{13}\text{C}^{14}\text{N}_2$, a été enregistré, dans la région allant de 12 à 250 GHz. A partir d'une analyse de la structure nucléaire hyperfine des transitions rotationnelles, on a déterminé les constantes de couplage quadrupolaire et les constantes rotationnelles de spin. En utilisant l'hamiltonien A -réduit de Watson, on a obtenu les constantes rotationnelles, les constantes de distorsion centrifuge d'ordre quatre, ainsi que quelques unes d'ordre six, pour l'état vibrationnel fondamental. Les constantes rotationnelles obtenues sont

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Les constantes de couplage quadrupolaire nucléaire et les constantes de spin-rotation sont

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pour les quadropoles des deux noyaux N identiques. La précision des constantes obtenues nous permet d'évaluer les positions de raies et la structure hyperfine de n'importe quelle transition dans la région des micro-ondes et des ondes millimétriques.

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Introduction

Within the framework of recent high-resolution studies of diazomethane, H_2CNN , and its isomers, the rotational and the infrared spectrum of the three-membered ring molecule diazirine has been studied. In analyzing the nuclear hyperfine structure of Q - and R -branch transitions of the main isotopic species $\text{H}_2^{12}\text{C}^{14}\text{N}_2$ in the ground vibrational state, it was found that the magnetic interactions as well as the nuclear quadrupole coupling of the two identical nitrogen nuclei could not be neglected (1). In the infrared region,

the rotational fine structure of the fundamental vibrational bands of the isotopomers $\text{H}_2^{12}\text{C}^{14}\text{N}_2$, $\text{H}_2^{12}\text{C}^{15}\text{N}_2$, $\text{D}_2^{12}\text{C}^{14}\text{N}_2$, and $\text{H}_2^{13}\text{C}^{14}\text{N}_2$ have been observed with medium (0.08 cm^{-1}) and Doppler-limited (0.005 cm^{-1}) resolution. The rotational and centrifugal distortion constants that were obtained for the isotopomer $\text{H}_2^{12}\text{C}^{14}\text{N}_2$ were used for the rovibrational analysis of the ν_3 and ν_7 fundamental bands in the infrared region (2, 3). In order to determine a precise substitution structure of the molecule, the rotational spectra of the isotopomers $\text{H}_2^{12}\text{C}^{14}\text{N}^{15}\text{N}$ and $\text{H}_2^{12}\text{C}^{15}\text{N}_2$ have also been

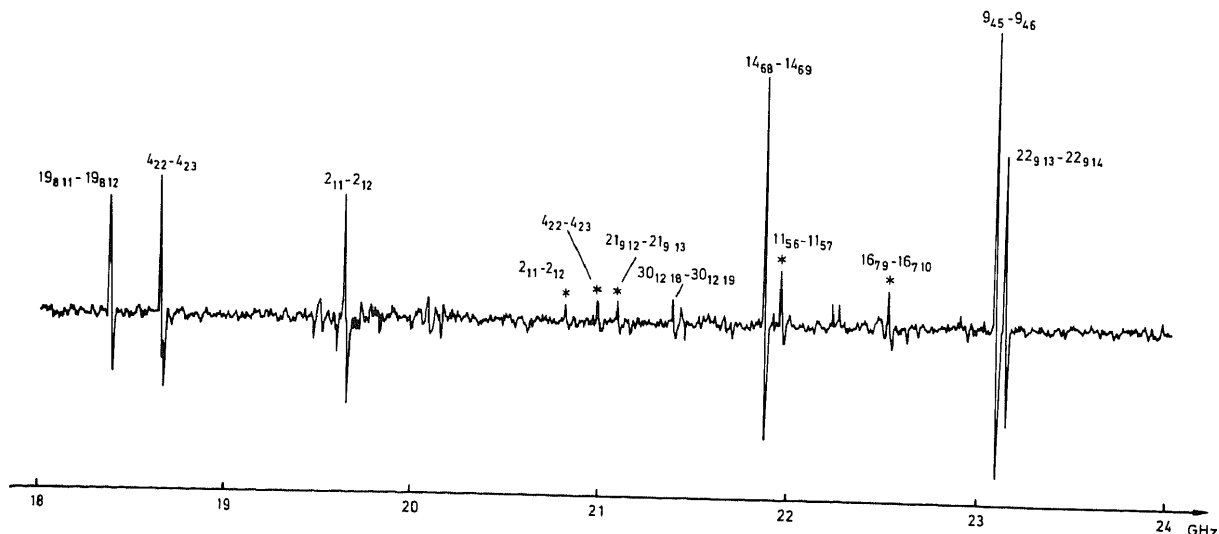


FIG. 1. Microwave spectrum of $\text{H}_2^{13}\text{C}^{14}\text{N}_2$ in the region between 18 and 24 GHz. The lines indicated by * belong to the parent species, $\text{H}_2^{12}\text{C}^{14}\text{N}_2$.

investigated (4).

In this paper we report the rotational spectrum of $\text{H}_2^{13}\text{C}^{14}\text{N}_2$, which has been measured in the microwave and millimetre wave region. The rotational and centrifugal distortion constants obtained in this study are mandatory for the analysis of the ^{13}C diazirine rovibrational spectrum, which is presently being carried out in our laboratory.

Experimental procedures

Isotopically enriched ^{13}C diazirine was prepared by means of a modification of the method of Ohme and Schmitz (4, 5). In this case, ^{13}C -enriched formaldehyde was used as a precursor (Merck, Sharp and Dohme, Canada). Diazirine is rather stable in the gaseous phase, but may explode in the liquid phase (4) when a liquid–solid phase transition occurs.

The microwave spectrum was recorded with a Hewlett-Packard molecular rotational resonance (MRR) spectrometer, Model 8460 A, between 12.4 and 40.0 GHz, whereas the spectra between 100 and 250 GHz were measured with the millimetre wave spectrometer that has been described elsewhere (6–9). By using a programmable, digitally swept frequency synthesizer (model SMPC, Rohde und Schwarz), which also can be operated with internal frequency modulation, some components of the previous frequency standard could be replaced. During the digital sweep a linear voltage between 0 and 5 V, generated by the synthesizer, has been used to provide a linear frequency axis for an x - y recorder. Consequently, a digitally stepped line profile results. In order to resolve the hyperfine structure of the rotational transitions, while

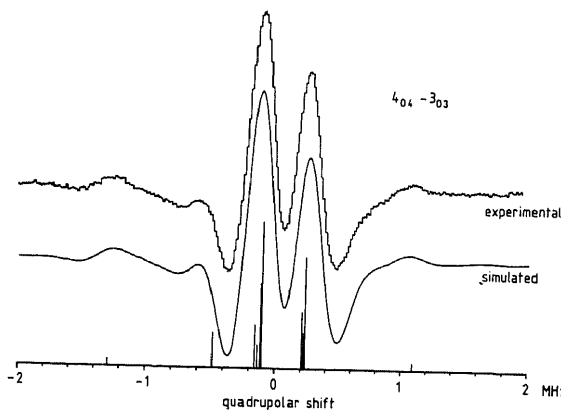


FIG. 2. Simulation of the hyperfine structure of the transition $4_{04}-3_{03}$ at 145 046.4199 MHz. (The line width was adjusted empirically to 0.310 MHz in order to reproduce the observed multiplet.)

presenting a well-defined line-shape for comparison with simulated transitions, source modulation of the klystron at a modulation frequency of 4.5 kHz was applied with a frequency excursion of 1 kHz for recording most of the lines. The signal was processed by using a second-harmonic lock-in detection at 9 kHz, which gives the second derivative of the frequency-modulated line profile. In all of these experiments the typical sample pressure in the absorption cell was below 1 Pa, so that Doppler line widths were recorded.

In Fig. 1, the microwave spectrum of ^{13}C isotopically enriched diazirine recorded with the Stark spectrometer is shown between 18 and 24 GHz. A comparison of the

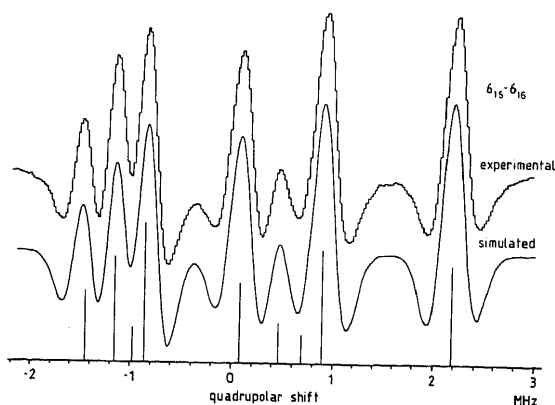


FIG. 3. Simulation of the hyperfine structure of the transition $6_{15}-6_{16}$ at 122 730.8586 MHz (line width: 0.275 MHz).

relative intensities of the transitions $2_{11}-2_{12}$ and $4_{22}-4_{23}$ for the ^{13}C -containing isotopomer and the main isotopic species leads to a relative abundance of 88.6% for $\text{H}_2^{13}\text{C}^{14}\text{N}_2$.

Rotational spectrum, hyperfine structure, and assignment

Like the main isotopic species, $\text{H}_2^{13}\text{C}^{14}\text{N}_2$ belongs to the symmetry point group C_{2v} . The total dipole moment lies along the symmetry axis, which is the axis of least moment of inertia. Consequently, only a -type rotational transitions could be expected. Since the rotational and centrifugal distortion constants of $\text{H}_2^{12}\text{C}^{14}\text{N}_2$ (1), $\text{H}_2^{12}\text{C}^{14}\text{N}^{15}\text{N}$ (4), and $\text{H}_2^{12}\text{C}^{15}\text{N}_2$ (4) are well known, a rather reliable estimate of the appropriate molecular parameters could be made for $\text{H}_2^{13}\text{C}^{14}\text{N}_2$. A further criterion for assignment was the form of the hyperfine patterns, which are quite characteristic for different branches, especially for low J values.

The observed quadrupolar patterns are quite similar to those discussed for the main isotopic species (1). Owing to the additional spin contribution of the ^{13}C nucleus with $I = 1/2$, however, the spin statistics and, therefore, the intensities of the transitions as compared with the parent species are modified. The derived statistical weights are 42 for the oo and oe and 30 for the ee and eo rotational levels; otherwise the analysis followed exactly as in ref. 1. As with the main isotopic species, spin-rotational interactions must be taken into account in order to reproduce the recorded line shapes.

Figures 2–4 represent typical observed line profiles of low- J transitions in different branches. Only a few aR transitions exhibit distinct hyperfine splittings: $K_a = 0$ or 2 and $K_a + K_c = J''$ for $J'' \leq 3$ lead to more or less resolvable multiplet patterns, whereas $K_a = 1$, $J'' \leq 5$ show single lines at the unperturbed frequencies with

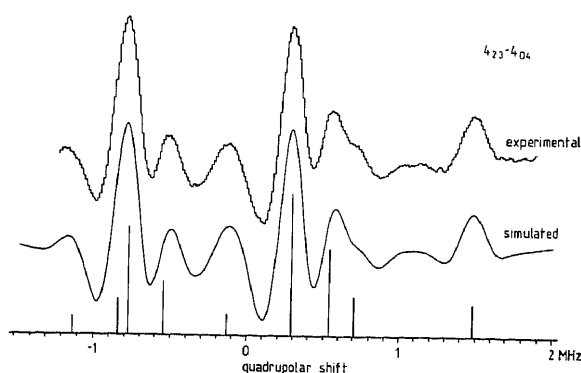


FIG. 4. Simulation of the hyperfine structure of the transition $4_{23}-4_{04}$ at 102 918.5057 MHz (line width: 0.220 MHz).

small side components for $K_a + K_c = J'' + 1$. In Fig. 2, the transition $4_{04}-3_{03}$ is the best example of the above-mentioned multiplets. Most of the hyperfine components superimpose to form an intense doublet-type absorption feature, whereas the remaining components form weak lines that can just be distinguished from the base line.

In contrast to the aR -branch transitions, the multiplet patterns of the aQ -branch lines are much more spread out. These multiplets could be observed up to $J'' \leq 25$ and $K_a = 10$. Lines with higher J'' values exhibit only slight shoulders in their line profiles. Figure 3 presents a well-resolved multiplet pattern of the transition $6_{15}-6_{16}$.

Owing to the asymmetry of the molecule, three transitions of the sQ_0 -branch could be observed. They also exhibit a characteristic multiplet structure; one of these transitions ($4_{23}-4_{04}$) is represented in Fig. 4. With increasing J values, the multiplet contracts to a triplet.

The hyperfine components of all transitions used in the analysis are given in Table 1. In all, 17 aR -, 31 aQ -, and 3 sQ_0 -branch transitions could be assigned for the ground vibrational state. The adjusted nuclear quadrupole and spin-rotational constants are given in Table 2. Since the principal coordinates of the nuclei in this isotopomer differ only slightly from those in the parent species, the nuclear quadrupole coupling and the spin-rotational constants should not be affected upon ^{13}C substitution. Indeed, within the error limits, these parameters coincide with those obtained for the parent species (1).

Centrifugal distortion analysis

In order to determine the rotational and centrifugal distortion constants, the unperturbed frequencies were obtained by the simulation of the multiplet pattern for each transition (see Table 1) as demonstrated in the previous paper (1). For the unresolved aQ transitions in

TABLE I. Calculated and observed unperturbed rotational transitions, and their nuclear quadrupole hyperfine components and theoretical relative intensities for $H_2^{13}C^{14}N_2$ in the ground vibrational state

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs. (MHz)	obs.-calc. (MHz)	obs. maxima (MHz)	quadrupolar shift (MHz)	rel. int. (%)	F'	I'_{12}	F''	I''_{12}
1(0, 1) - 0(0, 0)	39192.3880	0.0215							
4(0, 4) - 3(0, 3)	145046.4199	-0.0018	-1.2767	-1.2944	5.1	3	1	3	1
				-0.4841	24.1	4	2	3	2
				-0.1524	30.0	5	2	4	2
			-0.1303	-0.1338	16.2	3	2	2	2
				-0.1116	58.4	3	1	2	1
				-0.1045	100.0	5	1	4	1
				0.2112	39.4	6	2	5	2
				0.2150	25.4	4	0	3	0
				0.2227	11.7	2	2	1	2
			0.2385	0.2349	76.7	4	1	3	1
			1.0614	1.0971	5.1	4	1	4	1
5(0, 5) - 4(0, 4)	177096.6130	-0.0004							
6(0, 6) - 5(0, 5)	209179.8830	0.0826 *							
7(0, 7) - 6(0, 6)	241495.3758	0.0035							
3(1, 3) - 2(1, 2)	106914.5732	0.0710 *							
4(1, 4) - 3(1, 3)	141247.4920	0.0146							
5(1, 5) - 4(1, 4)	174920.5160	-0.0084							
5(1, 4) - 4(1, 3)	203620.3416	-0.0196 *							
6(1, 6) - 5(1, 5)	208117.2459	-0.0036							
7(1, 7) - 6(1, 6)	241024.3813	0.0053							
3(2, 2) - 2(2, 1)	117571.7393	0.0063		-0.2925	9.7	3	2	2	2
				-0.2753	11.8	3	0	2	2
				-0.2072	7.8	3	2	3	2
				-0.1842	27.8	4	2	3	2
				-0.1638	46.7	2	1	1	1
			-0.0950	-0.0701	8.6	3	1	3	1
				-0.0471	100.0	4	1	3	1
				0.0670	5.6	4	2	4	2
				0.0957	40.7	5	2	4	2
			0.1330	0.1517	8.6	2	1	2	1
				0.1625	5.2	1	2	1	2
				0.1689	69.1	3	1	2	1
				0.1740	10.4	2	2	1	2
				0.2121	8.1	3	2	2	0
				0.2294	14.1	3	0	2	0
				0.3371	5.2	1	2	0	2
3(2, 1) - 2(2, 0)	123050.8558	-0.0134							
4(2, 3) - 3(2, 2)	155594.5041	-0.0009							
5(2, 3) - 4(2, 2)	211321.2430	-0.0058							
6(3, 3) - 5(3, 2)	247931.4500	-0.0232							
6(4, 3) - 5(4, 2)	239873.4230	0.0104							
2(1, 1) - 2(1, 2)	19639.9060	-0.0144		-2.3659	13.3	1	2	0	2
				-2.2085	13.3	0	2	1	2
				-1.9909	41.0	2	0	2	0
			-1.8145	-1.8021	10.0	1	2	2	0
				-1.7176	10.1	2	0	1	2
				-1.5167	15.4	2	1	2	1
			-0.8530	-0.8528	100.0	4	2	4	2
				-0.3289	11.6	3	2	2	0
				0.0679	11.5	2	0	3	2
			0.2797	0.2785	20.0	3	2	4	2
				0.3375	13.2	2	2	1	2
				0.4386	27.7	3	1	3	1
				0.5986	20.0	4	2	3	2
				0.7641	13.3	1	2	2	2
				1.5045	10.0	1	1	1	1
			1.8363	1.7299	46.7	3	2	3	2
				2.1229	15.1	2	2	3	2
			2.2533	2.2374	15.2	3	2	2	2
			2.6664	2.6305	34.1	2	2	2	2

TABLE I. (Continued)

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs. (MHz)	obs.-calc. (MHz)	obs. maxima (MHz)	quadrupolar shift (MHz)	rel. int. (%)	F' I' I' F'' I'' I''	
3(1, 2) - 3(1, 3)	39063.1011	0.0125	-2.4143	-2.4074	20.2	1 2 1 2	
			-1.6974	-1.7391	10.1	2 2 1 2	
				-1.7005	57.9	3 0 3 0	
				-1.4926	19.8	3 1 3 1	
				-1.3198	5.7	2 2 3 0	
				-1.2822	10.1	1 2 2 2	
				-0.9945	5.8	3 0 2 2	
				-0.9866	-0.9750	100.0	5 2 5 2
					-0.6139	25.3	2 2 2 2
					-0.5163	6.0	4 2 3 0
					-0.0865	11.1	4 2 5 2
					0.3084	6.0	3 0 4 2
					0.5056	28.4	4 1 4 1
				0.5446	0.6041	11.1	5 2 4 2
					0.6536	9.4	3 2 2 2
					1.1797	15.0	2 1 2 1
				1.4941	1.4926	64.0	4 2 4 2
					1.5163	9.4	2 2 3 2
					1.9566	9.7	3 2 4 2
					2.3199	9.8	4 2 3 2
		2.7856	2.7838	50.5	3 2 3 2		
6(1, 5) - 6(1, 6)	122730.8586	-0.0016	-1.4869	-1.4454	51.2	4 2 4 2	
			-1.1518	-1.1524	75.5	6 0 6 0	
				-1.1116	25.2	6 1 6 1	
				-0.8572	-0.8584	100.0	8 2 8 2
				0.0691	0.0791	58.0	5 2 5 2
				0.4642	0.4581	29.9	7 1 7 1
					0.6889	21.7	5 1 5 1
				0.9055	0.8970	82.3	7 2 7 2
				2.1900	2.1736	71.9	6 2 6 2
			7(1, 6) - 7(1, 7)	152094.4707	0.0019		-1.1873
	-0.9649	78.3				7 0 7 0	
	-0.9392	26.1				7 1 7 1	
	-0.7495	-0.7419				100.0	9 2 9 2
	0.2086	0.1229				63.3	6 2 6 2
		0.4007				30.2	8 1 8 1
		0.5596				23.0	6 1 6 1
	0.7990	0.7272				84.9	8 2 8 2
	1.9502	1.8446				75.6	7 2 7 2
4(2, 2) - 4(2, 3)	18648.5940	-0.0196					-1.0399
				-0.7783	25.5	4 0 4 0	
				-0.6898	-0.7205	76.9	4 1 4 1
					-0.5133	38.3	6 2 6 2
					-0.1114	15.6	3 2 3 2
				0.3060	0.2665	100.0	5 1 5 1
					0.5077	62.1	3 1 3 1
					0.6564	28.0	5 2 5 2
5(2, 3) - 5(2, 4)	37296.9379	-0.0035		1.3772	23.2	4 2 4 2	
					-1.1812	16.6	3 2 3 2
					-0.9193	27.0	5 0 5 0
				-0.8630	-0.8737	81.3	5 1 5 1
					-0.6556	37.7	7 2 7 2
					-0.1220	19.1	4 2 4 2
				0.3734	0.3431	100.0	6 1 6 1
					0.5723	68.4	4 1 4 1
					0.7426	29.6	6 2 6 2
				1.7196	1.6974	25.4	5 2 5 2
9(2, 7) - 9(2, 8)	158683.2760	0.0019			-0.9630	23.4	7 2 7 2
					-0.8063	29.8	9 0 9 0
				-0.7905	-0.7928	89.4	9 1 9 1
					-0.6492	36.2	11 2 11 2
					0.1669	25.6	8 2 8 2
				0.3723	0.3536	100.0	10 1 10 1
					0.4493	80.8	8 1 8 1
					0.5764	32.0	10 2 10 2
				1.5378	1.5660	29.1	9 2 9 2

TABLE I. (Continued)

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs. (MHz)	obs.-calc. (MHz)	obs. maxima (MHz)	quadrupolar shift (MHz)	rel. int. (%)	F' I' I'' I''	F'' I'' I'' I''			
10(2, 8) - 10(2, 9)	190322.3839	0.0064	-0.6843	-0.8215	24.3	8	2	8	2	
				-0.6925	30.1	10	0	10	0	
				-0.6832	90.4	10	1	10	1	
				-0.5636	36.0	12	2	12	2	
				0.1604	26.4	9	2	9	2	
			0.3427	0.3110	100.0	11	1	11	1	
				0.3786	82.5	9	1	9	1	
				0.4860	32.2	11	2	11	2	
				1.3692	1.3512	29.5	10	2	10	2
				6(3, 3) - 6(3, 4)	14691.3310	-0.0214	-0.3484	-0.5216	51.2	4
-0.4182	75.3	6	0					6	0	
-0.4035	25.2	6	1					6	1	
-0.3147	100.0	8	2					8	2	
0.0310	58.0	5	2					5	2	
0.2360	0.1649	29.9	7				1	7	1	
	0.2520	21.7	5				1	5	1	
	0.3248	82.3	7				2	7	2	
	0.7827	0.7899	72.2				6	2	6	2
	7(3, 4) - 7(3, 5)	30983.9819	0.0161				-0.5495	-0.7156	56.7	5
-0.5858				77.8	7	0		7	0	
-0.5705				26.1	7	1		7	1	
-0.4564				100.0	9	2		9	2	
0.0786				63.3	6	2		6	2	
0.0929				0.2409	30.2	8	1	8	1	
				0.3433	23.0	6	1	6	1	
				0.4401	84.9	8	2	8	2	
				1.1109	1.1218	75.6	7	2	7	2
				10(3, 7) - 10(3, 8)	119950.6029	0.0001	-0.7348	-0.9117	67.5	8
-0.7739	83.7	10	0					10	0	
-0.7633	27.9	10	1					10	1	
-0.6358	100.0	12	2					12	2	
0.1831	73.3	9	2					9	2	
0.1718	0.3447	30.9	11				1	11	1	
	0.4264	25.5	9				1	9	1	
	0.5171	89.6	11				2	11	2	
	1.5080	1.5109	82.2				10	2	10	2
	11(3, 8) - 11(3, 9)	156903.4927	-0.0052				-0.7119	-0.8497	70.0	9
-0.7255				85.0	11	0		11	0	
-0.7172				28.3	11	1		11	1	
-0.6011				100.0	13	2		13	2	
0.1862				75.6	10	2		10	2	
0.4405				0.3295	31.0	12	1	12	1	
				0.3933	26.0	10	1	10	1	
				0.4987	90.6	12	2	12	2	
				1.4213	1.4212	83.7	11	2	11	2
				9(4, 5) - 9(4, 6)	23091.7269	0.0040	-0.3562	-0.4425	23.4	7
-0.3734	29.8	9	0					9	0	
-0.3673	89.4	9	1					9	1	
-0.3044	36.2	11	2					11	2	
0.0797	25.6	8	2					8	2	
0.1832	0.1621	100.0	10				1	10	1	
	0.2102	80.8	8				1	8	1	
	0.2658	32.0	10				2	10	2	
	0.7262	29.2	9				2	9	2	
	12(4, 8) - 12(4, 9)	107575.0290	0.0021				-0.6497	-0.7649	25.7	10
-0.6576				27.2	12	0		12	2	
-0.6533				92.0	12	1		12	1	
-0.5544				35.6	14	2		14	2	
0.1826				27.6	11	2		11	2	
0.3470				0.3026	100.0	13	1	13	1	
				0.3549	85.1	11	1	11	1	
				0.4454	32.5	13	2	13	2	
				1.3070	1.2941	27.2	12	2	12	0

TABLE I. (Continued)

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs. (MHz)	obs.-calc. (MHz)	obs. maxima (MHz)	quadrupolar shift (MHz)	rel. int. (%)	F' I' 12	F'' I'' 12	
13(4, 9) - 13(4, 10)	146958.1244	-0.0023	-0.6603	-0.7639	26.2	11 2	11 2	
				-0.6611	30.8	13 0	13 0	
				-0.6555	92.6	13 1	13 1	
				-0.5580	35.5	15 2	15 2	
				0.1918	28.0	12 2	12 2	
				0.3077	100.0	14 1	14 1	
				0.3510	86.1	12 1	12 1	
				0.4409	32.7	14 2	14 2	
				1.3018	30.5	13 2	13 2	
				11(5, 6) - 11(5, 7)	15805.0420	-0.0014	-0.1677	-0.2638
-0.2269	84.9	11 0	11 0					
-0.2243	28.3	11 1	11 1					
-0.1900	100.0	13 2	13 2					
0.0699	0.0595	75.6	10 2					10 2
0.1021	31.0	12 1	12 1					
0.1241	26.0	10 1	10 1					
0.1552	90.6	12 2	12 2					
12(5, 7) - 12(5, 8)	32112.8726	0.0095	-0.3408	-0.4055	72.1	10 2	10 2	
				-0.3508	86.0	12 0	12 0	
				-0.3475	28.7	12 1	12 1	
				-0.2962	100.0	14 2	14 2	
				0.0980	77.4	11 2	11 2	
				0.1669	0.1603	31.2	13 1	13 1
				0.1895	26.5	11 1	11 1	
				0.2364	91.4	13 2	13 2	
				0.6561	0.6896	85.0	12 2	12 2
				14(6, 8) - 14(6, 9)	21872.8300	-0.0001	-0.1893	-0.2582
-0.2257	31.0	14 0	14 0					
-0.2242	93.1	14 1	14 1					
-0.1933	35.3	16 2	16 2					
0.0692	28.4	13 2	13 2					
0.0957	0.1055	100.0	15 1					15 1
0.1196	87.0	13 1	13 1					
0.1482	32.7	15 2	15 2					
0.4454	30.7	14 2	14 2					
17(6, 11) - 17(6, 12)	108713.3667	0.0027	-0.5137					-0.5806
				-0.5104	31.4	17 0	17 0	
				-0.5079	94.3	17 1	17 1	
				-0.4402	35.0	19 2	19 2	
				0.1692	29.3	16 2	16 2	
				0.2538	0.2459	100.0	18 1	18 1
				0.2629	89.2	16 1	16 1	
				0.3267	32.9	18 2	18 2	
				1.0120	1.0102	31.2	17 2	17 2
				18(6, 12) - 18(6, 13)	152948.0651	-0.0022	-0.5478	-0.6181
-0.5433	31.5	18 0	18 0					
-0.5410	94.6	18 1	18 1					
-0.4686	35.0	20 2	20 2					
0.1831	29.5	17 2	17 2					
0.2690	0.2643	100.0	19 1					19 1
0.2774	89.7	17 1	17 1					
0.3457	33.0	19 2	19 2					
1.0882	1.0762	31.3	18 2					18 2
16(7, 9) - 16(7, 10)	14050.3280	-0.0028						
17(7, 10) - 17(7, 11)	28488.0640	0.0041	-0.1945	-0.2563	79.4	15 2	15 2	
				-0.2260	89.7	17 0	17 0	
				-0.2249	29.9	17 1	17 1	
				-0.1957	100.0	19 2	19 2	
				0.0839	0.0754	83.6	16 2	16 2
				0.1085	31.7	18 1	18 1	
				0.1169	28.3	16 1	16 1	
				0.1443	94.0	18 2	18 2	
				0.4475	89.1	17 2	17 2	

TABLE I. (Concluded)

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs. (MHz)	obs.-calc. (MHz)	obs. maxima (MHz)	quadrupolar shift (MHz)	rel. int. (%)	F' I' F'' I''
19(8,11) - 19(8,12)	18383.8010	-0.0089				
20(8,12) - 20(8,13)	35627.4910	0.0023				
				-0.2565	28.6	18 2 18 2
				-0.2271	31.7	20 0 20 0
				-0.2263	95.1	20 1 20 1
			-0.1755	-0.1977	34.8	22 2 22 2
				0.0797	29.9	19 2 19 2
			0.1024	0.1114	100.0	21 1 21 1
				0.1151	90.7	19 1 19 1
				0.1423	33.0	21 2 21 2
				0.4505	31.6	20 2 20 2
22(9,13) - 22(9,14)	23142.3180	0.0169				
24(10,14) - 24(10,15)	14398.8510	-0.0051				
25(10,15) - 25(10,16)	28314.3240	0.0029				
27(11,16) - 27(11,17)	17743.1540	-0.0140				
28(11,17) - 28(11,18)	33889.3640	-0.0081				
30(12,18) - 30(12,19)	21392.0570	0.0083				
33(13,20) - 33(13,21)	25340.4120	0.0017				
4(2, 3) - 4(0, 4)	102918.5057	0.0162				
			-1.1754	-1.1263	13.2	2 2 2 2
			-0.7949	-0.8334	25.5	4 0 4 0
				-0.7718	76.9	4 1 4 1
			-0.5266	-0.5372	38.3	6 2 6 2
			-0.1323	-0.1292	15.6	3 2 3 2
			0.2845	0.2907	100.0	5 1 5 1
			0.5515	0.5355	62.1	3 1 3 1
				0.7047	28.0	5 2 5 2
			1.4723	1.4743	23.1	4 2 4 2
5(2, 4) - 5(0, 5)	118494.7753	-0.0219				
			-1.1967	-1.1234	16.6	3 2 3 2
				-0.8662	27.0	5 0 5 0
			-0.8372	-0.8233	81.3	5 1 5 1
			-0.5865	-0.6073	37.7	7 2 7 2
			-0.0635	-0.0193	19.1	4 2 4 2
			0.3397	0.3278	100.0	6 1 6 1
			0.5358	0.5328	68.4	4 1 4 1
				0.7018	29.6	6 2 6 2
			1.6038	1.5956	25.3	5 2 5 2
6(2, 5) - 6(0, 6)	138013.0458	0.0062				
				-1.0683	19.1	4 2 4 2
				-0.8477	28.1	6 0 6 0
			-0.8199	-0.8177	84.3	6 1 6 1
				-0.6263	37.2	8 2 8 2
				0.0546	21.6	5 2 5 2
			0.3918	0.3392	100.0	7 1 7 1
				0.5038	72.8	5 1 5 1
				0.6611	30.6	7 2 7 2
			1.5998	1.5974	26.8	6 2 6 2

*Blended line, weighted by a factor of one-tenth.

TABLE 2. Nuclear quadrupole coupling and spin-rotation constants for $H_2^{13}C^{14}N_2$

$\chi_{aa} = -0.665(5)$ MHz	$C_{aa} = 11.1$ kHz*
$\chi_{bb} = -2.695(5)$ MHz	$C_{bb} = 6.1$ kHz*
	$C_{cc} = 0.0$ kHz*

*Constrained to the values of the parent species.

the microwave region, the unperturbed frequencies were derived by calculating the centre of gravity of the multiplet (10). These frequencies are given in Table 1. For the numerical analysis of the rotational (rot) transitions, Watson's *A*-reduced Hamiltonian (11) in the *I'*-axis representation was used.

$$H_{\text{rot}} = 1/2(B + C)\hat{P}^2 + \{A - 1/2(B + C)\hat{P}_a^2 - \Delta_J\hat{P}^4 - \Delta_{JK}\hat{P}^2\hat{P}_a^2 - \Delta_K\hat{P}_a^4 + 1/2[(1/2(B - C) - \delta_J\hat{P}^2 - \delta_K\hat{P}_a^2), (\hat{P}_+^2 + \hat{P}_-^2)]_+ + H_{JK}(\hat{P}^2)^2\hat{P}_a^2 + H_{KJ}(\hat{P}^2)\hat{P}_a^4 + 1/2[h_J(\hat{P}^2)^2 + h_K\hat{P}_a^4, \hat{P}_+^2 + \hat{P}_-^2]\}_+$$

TABLE 3. Rotational and centrifugal distortion constants in the *A*-reduced Hamiltonian for diazirine isotopomers in the ground vibrational state*

		H ₂ ¹³ C ¹⁴ N ₂ †	H ₂ ¹² C ¹⁴ N ₂ ‡	H ₂ ¹² C ¹⁴ N ¹⁵ N§	H ₂ ¹² C ¹⁵ N ₂ §
<i>A</i>	(MHz)	40 950.3414(23)	40 951.3526(11)	39 798.966(79)	38 604.89635(99)
<i>B</i>	(MHz)	22 869.8200(10)	23 667.98345(46)	23 416.7922(91)	23 200.85858(61)
<i>C</i>	(MHz)	16 322.66702(93)	16 726.11565(35)	16 406.788(11)	16 095.59679(63)
Δ_J	(kHz)	30.116(13)	31.5651(22)	30.29(33)	30.101(10)
Δ_{JK}	(kHz)	103.145(52)	107.940(12)	102.6(41)	100.242(19)
Δ_K	(kHz)	-17.40(16)	-23.456(50)	-23.3(119)	-26.084(50)
δ_J	(kHz)	8.8737(18)	9.4407(12)	9.33(25)	9.28800(99)
δ_K	(kHz)	74.975(44)	77.179(13)	75.7(37)	73.7025(97)
H_{JK}	(Hz)	-0.551(70)	-0.56(12)	-0.54(16)	-0.794(14)
H_{KJ}	(Hz)	2.59(34)	2.77(16)	—	2.247(58)
h_J	(Hz)	-0.0108	-0.0108(33)	—	—
h_K	(Hz)	3.31	3.31(49)	—	—
σ	(kHz)	12.6	16.0	23.6	9.6
κ		-0.4683	-0.4269	-0.4007	-0.3687

* Figures in parentheses are standard deviations in units of the least significant figures.

† Present work.

‡ Reference 1.

§ Reference 4.

^{||} Held fixed during the fit.

where \hat{P} , \hat{P}_a , \hat{P}_b , and \hat{P}_c are the operators of the total angular momentum and its components along the principal inertial axes. The coefficients, *A*, *B*, and *C* are Watson's *A*-reduced rotational constants. Δ_J , Δ_{JK} , Δ_K , δ_J , and δ_K are quartic and H_{JK} , H_{KJ} , h_J , and h_K are sextic centrifugal distortion constants. A total of 51 transitions were fitted, three ⁹R transitions, which were measured by video-averaging, were weighted by a factor of one-tenth since the line shape could not be exactly simulated. The resulting molecular constants are presented in Table 3 together with the rotational and centrifugal distortion constants of all isotopomers of diazirine available so far.

As mentioned in the introduction, the adjusted spectroscopic constants reported in this paper are presently being used in the analysis of high-resolution infrared spectra. The evaluation of a reliable *r_s* structure for diazirine will follow as soon as the data of the deuterated isotopomers become available.

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